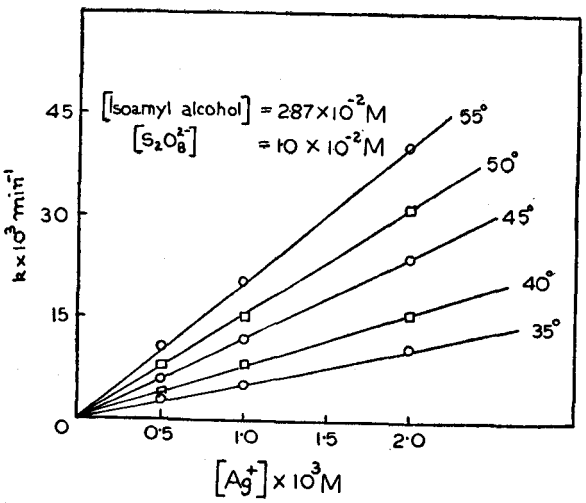

Fig. 1 — Effect of varying [Ag+] on the reaction rate at different temperatures

On the basis of results the rate law may be represented by Eq. (1)

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_r[S_2O_8^{2-}][Ag^+] \quad ...(1)$$

where k_r is the specific rate constant and comes out to be $k/[Ag^+]$ litres mole^{-1} min^{-1}.

The results obtained might be explained on proposing the mechanism given in Scheme 1.

$$S_2O_8^{2-} + Ag^+ \xrightarrow{k_1} Ag^{2+} + SO_4^{\cdot-} + SO_4^{2-} \quad ...(2)$$

$$SO_4^{\cdot-} + Ag^+ \xrightarrow{k_2} Ag^{2+} + SO_4^{2-} \quad ...(3)$$

$$RCH_2OH + Ag^{2+} \xrightarrow{k_3} R\dot{C}HOH + Ag^+ + H^+ \quad ...(4)$$

$$R\dot{C}HOH + S_2O_8^{2-} \xrightarrow{k_4} RCHO + SO_4^{2-} + SO_4^{\cdot-} + H^+ \quad ...(5)$$

$$R\dot{C}HOH + SO_4^{\cdot-} \xrightarrow{k_5} RCHO + HSO_4^- \quad ...(6)$$

where $(CH_3)_2CHCH_2 = R$

Scheme 1

This mechanism clearly explains the first order kinetics with respect to peroxydisulphate and Ag+ both. The various steps proposed are quite justified because in the Ag+-catalysed oxidations, Ag^{2+} and a number of free radicals as intermediates have been reported by several workers[8-14].

The rate of disappearance of peroxydisulphate may be given as,

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_1[S_2O_8^{2-}][Ag^+] + k_4[R\dot{C}HOH][S_2O^{2-}] \quad ...(7)$$

Considering the steady state conditions, the value of [RĊHOH] comes out to be

$$[R\dot{C}HOH] = \left(\sqrt{\frac{2k_1k_2}{k_4k_5} + \frac{k_2^2}{4k_5^2}} - \frac{k_2}{2k_5}\right)[Ag^+] \quad ...(8)$$

Apparently Eq. (8) shows quite complicated feature but the close examination clearly reveals that the whole factor consists of various constants along with the [Ag+] and hence it can be simplified as follows:

$$[R\dot{C}HOH] = \text{constant } [Ag^+] \quad ...(9)$$

On substituting the value of [RĊHOH] in Eq. 7 we get

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_1[S_2O_8^{2-}][Ag^+] + k_4.\text{constant. } [Ag^+]$$

$$= k_r[S_2O_8^{2-}]\,[Ag^+] \quad ...(10)$$

where $k_r = (k_1 + k_4.\text{ constant})$.

The above equation clearly explains the experimental results obtained at different conditions. The oxidation product, isopentanal was estimated from the reaction mixture and confirmed by its characteristic NMR spectrum.

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References

1. Tronov, B. V., Lukanin, A. A. & Pavlvinow, I. I. *J. Russ. phys. chem. Soc.*, **59** (1927), 1173.
2. Kirkhgaf, G. A., Korzina, O. I. & Astrova, R. Ya., *Chem. Abstr.*, **28** (1934), 3713.
3. Neznanov, A. G. & Levanevsku, O. E., *Chem. Abstr.*, **79** (1973), 4895z.
4. Knoerr, Fritz & Gunzenhauser, Werner, *Chem. Abstr.*, **78** (1973), 158947j.
5. Suga, T., Kihara, K. & Matsuura, T., *Bull. chem. Soc. Japan*, **38** (1965), 893.
6. Anantkrishnan, S. V. & Varadarajan, S., *Indian J. Chem.*, **10** (1972), 66.
7. Kolthoff, I. M. & Carr, E. M., *Analyt. Chem.*, **25** (1953), 298.
8. Srivastava, S. P. & Ghosh, S., *Proc. natn. Acad. Sci.*, **22** (1953), 91.
9. Bawn, C. R. H. & Margerison, D., *Trans. Faraday Soc.*, **51** (1955), 525.
10. Evans, M. G. & Baxendale, J. H., *Trans. Faraday Soc.*, **42** (1940), 195.
11. Higginson, W. C. & Marshall, J. W., *J. chem. Soc.*, (1957), 447.
12. Menghani, G. D. & Bakore, G. V., *Bull. chem. Soc. Japan*, **41** (1968), 2574.
13. Menghani, C. D. & Bakore, G. V., *Indian J. Chem.*, **7** (1969), 786.
14. Haber, F. & Weiss, J., *Proc. R. Soc.*, **A-147** (1934), 332.

Studies on Heteropoly Niobotungstate(VI)

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The nature and conditions of formation of heteropoly niobotungstate(VI) have been established with the help of pH and thermometric titrations. Based on chemical and physical studies, the compound has been formulated as $K_5Na_5[WNb_{12}O_{38}]11H_2O$. The molecular weight (2380) for the compound, determined from the unit cell dimensions, tallies with the formula weight. The pressure-composition isothermals studied in the solid phase at 35° and 45° indicated $K_5Na_5[WNb_{12}O_{38}]6H_2O$ to be the most stable form.

LAPITSKU and coworkers[1] reported a number of heteropoly niobate complexes of several transitional metal ions and also of Ce(III). Later Dale *et al.*[2] examined some of these complexes and in general found that the Russian work was not reproducible. In this note we report the results of

our studies on the heteropoly niobate complexes with tungsten.

Potassium hexaniobate was prepared following the literature method[3]. It analysed for $K_8Nb_6O_{19}.16H_2O$. Solutions of $M/50$ K-hexaniobate and $M/20$ sodium tungstate ($Na_2WO_4.2H_2O$, BDH grade), were prepared and found to be suitable for the present study. When $M/50$ potassium hexaniobate solution was gradually added to 60 ml of $M/20$ sodium tungstate, there was a gradual increase in pH of the solution up to the addition of 20 ml of K-hexaniobate. It was followed by a plateau of constant pH up to 30 ml of potassium hexaniobate. Thermometric titrations[4] corroborated the above results. By comparing these two curves, the range in volume of the reactants could be studied. A portion (30 ml) of $M/50$ K-hexaniobate was refluxed with 60 ml of $M/20$ sodium tungstate for 1 hr; the molar ratio between WO_4^{2-} and $Nb_6O_{19}^{8-}$ was 5:1. The reaction mixture was concentrated and left overnight when transparent of the complex separated out, which were recrystallized from hot water.

The complete analysis of the compound was done by chemical and instrumental methods. For the estimation of niobium and tungsten by chemical methods, niobium in the complex was separated by precipitation as niobic acid by adding ammonium-magnesium salt solution[5] and estimated as Nb_2O_5. In the filtrate tungsten was estimated as WO_3 using of tannin and cinchonine hydrochloride[6]. The analytical values were checked up by colorimetric determinations[7]. Sodium and potassium in the compounds were estimated by Zn-uranyl acetate and perchloric acid methods[8] respectively and the results fairly agreed with the results of flame photometric analysis. The percentages of water and oxygen were calculated by difference. The observed percentage composition of the compound came out to be W, 7·56; Nb, 46·25; Na, 4·67; K, 8·00; (water+oxygen) = 33·52 against the theoretical values 7·61, 46·16, 4·75, 8·00 and 33·137 respectively for $Na_5K_5[WNb_{12}O_{38}].11H_2O$. From the percentage composition, the W/Nb atomic ratio was calculated to be 1: 11·8. The excess of tungsten, taken in the beginning, was found in the mother liquor after crystallization.

For assigning the molecular formula, niobium and tungsten's projection pattern with oxygen, giving rise to the complex anion $[WNb_{12}O_{38}]^{10-}$ was taken into consideration[9]. From the atomic ratio of Nb: O, the percentage of oxygen came out to be 25·17, and hence the percentage of water was found to be 8·27. Thus, according to stoichiometric composition, the molecular formula of the compound could be represented as $Na_5K_5[WNb_{12}O_{38}].11H_2O$. Following IUPAC system of nomenclature the compound has been named as 12-heteropoly niobotungstate(VI).

Determination of pressure-composition isothermals — Use was made of the apparatus described by Bhattacharya and Sinha[10]. The isothermal (Fig. 1) at 35° showed loss of water molecules in two steps. In the first two water molecules are lost giving rise to a product containing 9 water molecules. In the second step 3 more water molecules are lost giving rise to a product containing 6 water molecules.

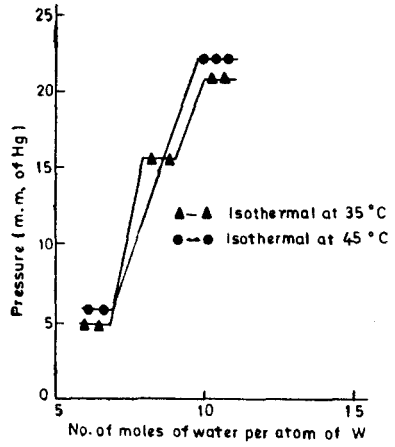

Fig. 1 — Isothermals of heteropoly niobotungstate(VI) at 35° and 45°

Thereafter no water molecules are lost. The isothermal at 45° did not show any stepwise dissociation but the end product on analysis showed the existence of $6H_2O$. These observations indicate that between 35° and 45° only $6H_2O$ remain as bound water molecules.

X-ray crystal diffraction — The compound, recrystallized as long needles from hot water, was used for X-ray studies. The unit cell dimensions were determined using rotation and Weissenberg photographs. The crystal data found were: $a = b = 9{\cdot}562$ Å; $c = 12{\cdot}28$ Å and $\alpha = \beta = 90°$; $\gamma = 120°$. The lattice was determined to be hexagonal. The volume V per unit cell calculated from the expression $3.\sqrt{3}/2.a^2.c$ was found to be 2918 Å^3. The observed density ($\rho_{obs.}$) for the compound determined by displacement method was found to be 2·705 g/ml. From the determination of space group, the number of unit cell n contained was fixed to be 2. Putting the above data in the expression $\rho_{obs.} = 1{\cdot}66\ M.n/V$ the molecular weight (M) of the compound was calculated to be which 2380 compared well with value 2415·2.

Generally it is believed that for a condensation process resulting in heteropoly compounds, it is necessary to maintain acidic medium[11]. However, in the present study the formation of $K_5Na_5[WNb_{12}O_{38}]11H_2O$ took place in the basic medium (pH 11·5). The formation in the presence of the OH^- ions may be compared with the catalytic behaviour of the OH^- ions in the base-catalysed aldol condensation. It may be predicted that in the formation of this type of heteropoly compound, OH^- ions behave as catalyst and the resultant compound might be the polyhedra of the oxides of niobium and tungsten resulting from the elimination of H_2O molecules. It is pertinent to mention that Lindqvist and workers[9] from their X-ray studies on isopoly anion $(NbO_{19})^{8-}$ pointed out a sort of projection pattern of niobium and oxygen.

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References

1. Lapitskŭ, A. V., Vlasov, K. G. & Bezrukov, V. I., *Dokl. Acad. Nauk. USSR*, **154** (1964), 868.

2. DALE, W. B., BUCKLEY, JANET M & POPE, M. T., *J. chem. Soc.*, **2A** (1969), 301.
3. MILLER, G. L., *Metallurgy of the rare earth metals*, Vol. VI (Butterworths, London), 1959, 68.
4. TYRELL, H. J. V. & BECZER, A. F., *Thermometric titrimetry* (Chapman & Hall, London), 1968), 58.
5. POWELL, A. R., SCHOLLER, W. R. & JOHN, C., *Analyst*, (1935), 506.
6. VOGEL, A. R., *A text book of quantitative inorganic chemistry* (Longmans, Green, London), 1960, 648-664.
7. SNELL, F. D. & SNELL, C. T., *Colorimetric analysis* (D. Van Nostrand), 1966, 339.
8. SCOTT, W. WILFRED & FURMAN, HOWELL N., *Standard methods of colorimetric analysis*, Vol. I (Technical Press Ltd, London), 1958, 871.
9. LINDQVIST, I., *Chem. Abstr.*, **47** (1953), 728a; **48** (1954), 9782i.
10. BHATTACHARYA, G. C. & SINHA, P. C., *J. Indian chem. Soc.*, **32** (1955), 317.
11. BHATTACHARYA, G. C. & ROY, S. K., *J. Indian chem. Soc.*, **50** (1973), 359.

Nb(III) Trisoxinate & Niobyl Phosphoniobate

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Niobium(III) oxinate and the complex phosphate containing Nb(III) have been isolated in an atmosphere of nitrogen and their analytical, spectral and magnetic data are reported. Both the compounds are susceptible to atmospheric oxidation.

WE have reported earlier the isolation and characterization of potassium disulphatoniobate (III) tetrahydrate in the solid state, the first really stable niobium compound in the trivalent state[1]. This has also been employed as a standard analytical reductant[2]. The present note describes the characterization of two other solid Nb(III) compounds viz., the niobium trisoxinate and a niobium phosphate.

Fluka's 99·8% niobium pentoxide was used in the experiments. All other reagents were of appropriate purity. The infrared spectra were recorded in KBr pellets in a Beckman IR 20 infrared spectrophotometer. Magnetic measurements were done in a Guoy balance. For potentiometric measurements a Cambridge portable *p*H meter was used.

Niobium(III)trisoxinate[$Nb^{III}(oxin)_3$]—8-Hydroxyquinoline (300 mg) was added to 100 mg of potassium disulphatoniobate(III) tetrahydrate[1] in 10 ml of 3*M* sulphuric acid. The mixture was neutralized with a saturated aqueous solution of $NaHCO_3$ till a flocculant precipitate of the oxinate appeared. The mixture was kept well stirred for 1 hr and the precipitate filtered in a sintered bed, washed thoroughly with water and dried by the passage of hot nitrogen. The entire operation was carried out in a specially designed all glass apparatus in an air-free condition and a slow stream of nitrogen was passed through the system throughout. The dry solid was then collected and stored under nitrogen. All reagents and wash liquid were previously made air-free.

For analysis, a weighed quantity of the compound was digested for a few hours with 6*M* hydrochloric acid with free access of air. The coagulated hydrated Nb_2O_5 was filtered off and 8-hydroxyquinoline hydrochloride was determined in the filtrate by titration with standard potassium bromate solution in the presence of KBr[3]. The hydrated Nb_2O_5 was ignited and weighed. For the determination of the oxidation number of niobium, weighed quantity of the compound was taken in an anaerobic condition and a few ml of 4*N* HCl was added to it. Standard iodine solution was then added to the solution, the mixture shaken for several hours and the excess iodine back titrated with sodium thiosulphate. It was checked beforehand that iodine did not react with free oxine under this condition. The oxidation number of niobium in the compound was found to be +3 [Found: Nb, 17·2; oxine, 81·3; oxidation number, 2·90, 2·88. $Nb(oxin)_3$ requires Nb, 17·7; oxine, 82·3%].

Niobium(III) oxinate is a deep violet solid insoluble in ethanol, acetone and benzene. It is weakly paramagnetic in nature (after correction for ligands, its μ_{eff} value has been found to be 0·76 BM at 30°). It is quantitatively oxidized to the yellow niobium(V) oxide trisoxinate[4] in aqueous suspension or even on exposure to atmospheric oxygen. The oxidation reaction is further confirmed by the infrared spectral data. The spectrum of Nb(III) oxinate is completely devoid of any Nb = O band which appears with increasing intensity on gradual exposure of the compound to atmospheric oxygen suggesting the reaction to be

$$Nb(oxin)_3 \xrightarrow{O_2} NbO(oxin)_3$$

Other characteristic infrared active bands (Table 1) of the oxinate are strikingly similar to other trivalent metal oxinate compounds[5].

Niobyl phosphoniobate(III) hexahydrate, $Nb^{V}O[Nb^{III}(PO_4)_2].6H_2O$ — Potassium disulphatoniobate-(III) tetrahydrate (100 mg) in 3*M* sulphuric acid (10 ml) was added to a mixture of 0·5 ml of glacial phosphoric acid and Na_2CO_3 (2 g) in water (50 ml). The mixture was neutralized with saturated Na_2CO_3

TABLE 1 — IR BANDS (cm^{-1}) OF NIOBIUM COMPOUNDS IN KBr

$Nb^{III}(oxin)_3$

3200 (m), 3030 (w), 1600 (w), 1570 (s), 1490 (s), 1455 (s), 1420 (w), 1370 (s), 1315 (s), 1270 (s), 1235 (w), 1170 (w), 1100 (s), 1030 (w), 815 (s), 800 (m), 780 (s), 740 (s)

$Nb^{V}O(oxin)_3$

3060 (w), 3020 (w), 1600 (w), 1585 (w), 1565 (s), 1485 (s), 1455 (s), 1415 (m), 1365 (s), 1310 (s), 1260 (s), 1215 (m), 1170 (m), 1100 (s), 1045 (w), 1020 (w), 905 (s), 890 (w), 835 (w), 820 (s), 800 (w), 790 (m), 730 (s), 620 (w), 610 (w), 510 (m), 490 (m)

$Nb^{V}O[Nb^{III}(PO_4)_2].6H_2O$

3600-3100 (s), 1630 (s), 1270 (s), 1050-1000 (s), 940 (s), 760 (m), 620 (s), 560 (s)